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(71) Applicant: MOBIL OIL CORPORATION
150 East 42nd Street
New York New York 10017(US)

(72) Inventor: Hagerty, Robert Olds
328 Horizon Drive
Edison New Jersey 08817(US)

(74) Representative: West, Alan Harry
Mobil Court 3 Clements Inn
London WC2A 2EB(GB)

(54) Process for removal of residual monomers from ethylene copolymers.

(57) Residual monomer is removed from copolymers of ethylene and higher olefins prepared in the gas phase by subjecting the copolymers to reduced pressure, sweeping the copolymers with reactor gas in the absence of inert gas and recycling the reactor gas containing residual monomers to the polymerization zone. This method avoids the use of an inert sweep gas (e.g. nitrogen) and the step of separating the residual monomer from the inert gas.

EP 0 127 253 A1

Croydon Printing Company Ltd.

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Title: PROCESS FOR REMOVAL OF RESIDUAL MONOMERS FROM ETHYLENE COPOLYMERS

This invention relates to a process for removal of residual monomers from ethylene copolymers.

Polymerization of monomers generally results in a polymer containing residual monomers which must be removed for economic reasons, to meet quality standards, or to satisfy regulatory requirements. In the copolymerization of ethylene and higher olefins resulting in so-called "linear low density polyethylene" residual monomers remain and can be removed by sweeping the copolymer with an inert gas such as nitrogen. Such a process is described in, for example, U.S. Patent 4,372,758. If it is desired to recycle the monomers to the polymerization reactor, the monomers must first be separated from the inert gas. An object of the present invention is to eliminate the use of inert gas, and the need for its separation, in the removal of residual monomers from ethylene copolymers.

Accordingly, the invention resides in a process for removing residual monomer from a solid copolymer of ethylene prepared by the gas phase polymerization in a polymerization zone above atmospheric pressure of a reactor gas which includes ethylene and at least one higher olefin monomer, comprising subjecting said solid copolymer to a reduced pressure zone sufficient to desorb said higher olefin monomer, sweeping said copolymer with reactor gas or a component thereof which is substantially free of inert gases and recycling the resulting gas containing desorbed higher olefin to said polymerization zone.

The present process is particularly applicable to the removal of residual monomers from copolymers of ethylene and higher olefins prepared in the gas phase. Higher olefins containing 4 to 6 carbon atoms are

particularly suitable for gas phase reaction. The method of preparation of ethylene copolymers in a gas phase fluid bed reactor is described in U.S. Patent 4,011,382. In particular, suitable comonomers are the olefins containing 3 to 6 carbon atoms such as propylene, 1-butene, 1-pentene, 1-hexene, and 4-methyl-1-pentene. These monomers may be present as the sole comonomer with ethylene or two or more of the higher olefins can be copolymerized with ethylene. The present process is particularly advantageous in the removal of hexene monomer from copolymers of ethylene and hexene.

The polymerization of ethylene and higher olefins in the gas phase is generally conducted at pressures of 150 to 350 psi (10.3 to 24.1 bar), preferably 250 to 350 psi (17.2 to 24.1 bar). In order to remove residual monomer from the copolymer, the copolymer is subjected to a reduced pressure zone at a pressure sufficient to desorb the higher olefin monomer substantially. The pressure in the reduced pressure zone is generally a factor of 0.2 or less than the pressure in the polymerization zone and more preferably a factor of 0.15 to 0.075 of the polymerization pressure. For example, where the pressure in the polymerization reactor is 315 psia (21.8 bar) the pressure in the reduced pressure zone is about 32 psia (2.2 bar) or a factor of about 0.1 of the pressure in the polymerization zone.

A small flow of reactor gas is used to sweep the desorbed monomers from the copolymer to prevent an accumulation of heavy monomers that would act to reduce efficiency. The sweep gas is recycled to the reactor along with the desorbed monomers. It is not necessary that the sweep gas contain the same constituents as the reactor gas fed to the polymerization reactor. Sweep gas may contain any one of the constituents of the reactor gas in the absence of the other constituents. For example the sweep gas can comprise ethylene alone or hydrogen which is commonly fed to the reactor. However, the sweep gas is substantially free of added inert gases such as nitrogen. Thus, where the reactor gas itself contains inert gas such as nitrogen, the addition of more inert gas to the sweep gas should be avoided to prevent the buildup of undesired amounts of inert gas in the reactor.

Generally, the equilibrium solubility of the monomer in the copolymer is reduced in the low pressure zone to about 1/10th of its initial value allowing 90 percent desorption to occur. The 90 percent recovery level is a practical limit which avoids unacceptably high levels of heavy inerts in the reactor, which are recovered along with the monomers. Sufficient residence time in the low pressure zone must be provided for desorption. For example, with hexene, approximately 20 minutes is required to reach a desirable 85-90 percent desorption.

The invention is illustrated by the following examples.

EXAMPLE 1

The computer simulation of the overall production process was carried out to investigate effects on the reactor with dissolved gas recovery. The simulation is based on a 90 percent recovery of monomer in the production of a terpolymer resin of ethylene, propylene, and hexene, having a density of about 0.918. The monomer efficiency listed in Table 1 (weight units of monomer consumed per weight unit of monomer incorporated into the product) were determined. The overall efficiency is a weighted average of the separate monomer efficiencies.

TABLE 1

	MONOMER EFFICIENCY	
	Without Recovery	With Recovery
Ethylene	1.0109	1.0035
Propylene	1.1884	1.0556
Hexene	1.4378	1.1337
Overall	1.0413	1.0127

EXAMPLE 2

In a similar manner the computer simulation was made based on a 90 percent recovery figure and the production of a copolymer of ethylene and butene-1 having a density of 0.918. The monomer efficiencies are listed in Table 2.

TABLE 2

	MONOMER EFFICIENCY	
	Without Recovery	With Recovery
Ethylene	1.0105	1.0040
Butene	1.2858	1.0760
Overall	1.0342	1.0102

WHAT IS CLAIMED IS

1. A process for removing residual monomer from a solid copolymer of ethylene prepared by the gas phase polymerization in a polymerization zone above atmospheric pressure of a reactor gas which includes ethylene and at least one higher olefin monomer, comprising subjecting said solid copolymer to a reduced pressure zone sufficient to desorb said higher olefin monomer, sweeping said copolymer with reactor gas or a component thereof which is substantially free of inert gases and recycling the resulting gas containing desorbed higher olefin to said polymerization zone.

2. The process of claim 1 in which said polymerization is conducted at a pressure of 150 to 350 psi (10.3 to 24.1 bar) and said reduced pressure zone is maintained at a pressure which is a factor of 0.2 or less of the polymerization pressure.

3. The process of claim 1 in which said polymerization is conducted at a pressure of 250 to 350 psi and said reduced pressure zone is maintained at a pressure which is a factor of 0.15 to 0.075 of tne polymerization pressure.

4. The process of any preceeding claim 1 in which said higher olefin contains at least 5 carbon atoms.

5. The process of claim 4 in which said higher olefin contains 6 carbon atoms.

6. The process of claim 5 in which said higher olefin is 1-hexene.

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EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
A	EP-A-0 022 386 (SOCIETE CHIMIQUE DES CHARBONNAGE)		C 08 F 6/26 // (C 08 F 6/26 C 08 F 210/02)
A	EP-A-0 068 146 (BASF)		

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 08 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17-08-1984	BOLETTI C.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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